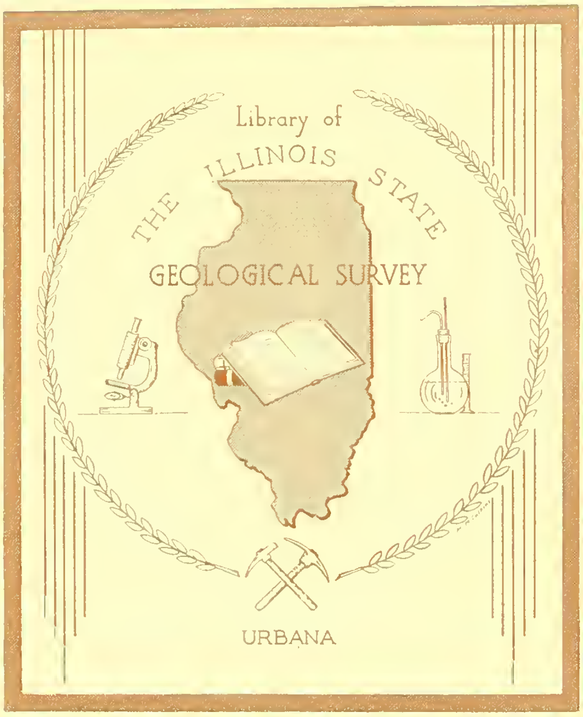

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STUDIES OF LAKE MICHIGAN BOTTOM SEDIMENTS—NUMBER TWO

DISTRIBUTION OF MAJOR, MINOR, AND TRACE CONSTITUENTS IN UNCONSOLIDATED SEDIMENTS FROM SOUTHERN LAKE MICHIGAN

Neil F. Shimp
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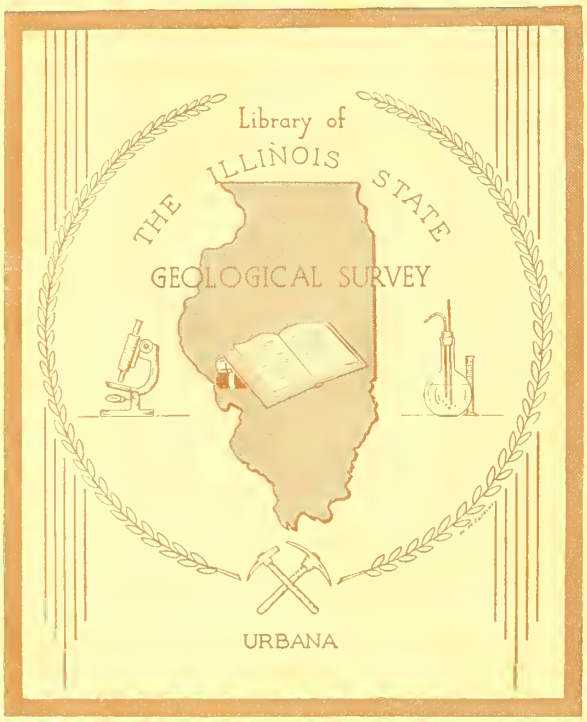
W. Arthur White

ILLINOIS STATE GEOLOGICAL SURVEY

JOHN C. FRYE, Chief • Urbana 61801



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STUDIES OF LAKE MICHIGAN BOTTOM SEDIMENTS—NUMBER TWO

DISTRIBUTION OF MAJOR, MINOR, AND TRACE CONSTITUENTS IN UNCONSOLIDATED SEDIMENTS FROM SOUTHERN LAKE MICHIGAN

Neil F. Shimp, Harry V. Leland, and W. Arthur White

ABSTRACT

Preliminary results from a study of the chemical composition of southern Lake Michigan sediments indicate that lead, bromine, zinc, nickel, and chromium accumulate in the upper few centimeters of these lake deposits. At this interval, concentrations of these elements appear to be related to the amount of organic carbon in the sediments. In deeper sediments, most trace element concentrations increase as the amount of less than 2-micron clay increases.

The two grab samples and four sediment cores analyzed in the Illinois State Geological Survey laboratories were subjected to X-ray fluorescence, neutron activation, optical emission, atomic absorption, and wet chemical methods. Major constituents determined were aluminum, silicon, iron, calcium, magnesium, potassium, sodium, inorganic carbon, and organic carbon. Titanium, manganese, phosphorus, and sulfur were found in smaller amounts. Trace elements determined were boron, beryllium, bromine, cadmium, cobalt, chromium, copper, lanthanum, nickel, lead, scandium, vanadium, and zinc. Amounts of less than 2-micron clay, clay mineral composition, acidity, and oxidation-reduction potential also were determined in the sediments at appropriate depth intervals.

INTRODUCTION

The second in a series of environmental geology notes on the basic geology and geochemistry of Lake Michigan bottom sediments, this report is a result of extensive cooperation between the Civil Engineering Department of the University of Illinois and the Illinois State Geological Survey. The

stratigraphy and clay mineralogy of sediments cored at 4-mile intervals along a line extending from 12 to 32 miles due east of Waukegan, Illinois, was described in the first report (Gross et al., 1970). Chemical analyses given in the present report further characterize the geology and geochemistry of sediments in southern Lake Michigan (fig. 1) and will be used to help clarify the relation of trace elements in the lake to recent environmental changes.

The sedimentary history and chemical composition of Lake Michigan sediments have received scant attention. However, environmental changes resulting from man's activities are taking place in localized areas of Lake Michigan. Large populations of pollution-tolerant sludgeworms, nourished by organic nutrients discharged into the lake by metropolitan centers, have been found in bottom sediments along the perimeter of the southern half of the lake (Fed. Water Pollution Control Adm., 1968a; Brinkhurst, 1967). Surface water run-off and industrial discharges appear to have contributed significant amounts of trace elements to the pollution of the Southern Lake Michigan Basin (Fed. Water Pollution Control Adm., 1968b). The oxygen demand of Lake Michigan sediments is about three times that of Lake Huron sediments, indicating organic enrichment in Lake Michigan (Beeton, 1968).

Little is known of the extent of accumulation of inorganic elements within Lake Michigan sediments, and this is especially true for toxic metals such as lead, copper, chromium, and cadmium. Until normal or baseline levels for these elements are determined, recent depositions cannot be evaluated. Such baselines are essential for distinguishing between natural variations in sediment and those due to the activities of man.

To establish baselines, complete chemical analyses of sediments from a wide area of Lake Michigan must be made, with both the uppermost sediments and the underlying older sediments included. Many variables are known to affect concentrations of elements in sediments, among them the amount of clay-size material present in the sediments, their mineralogic content, organic matter, acidity, and oxidation-reduction potential. These parameters were measured in this study to help in future evaluation of geochemical processes that operate during sedimentation.

METHODS

Lake sediment samples were obtained with a Shipek bucket (Hydroproducts, Inc., San Diego, Calif.) or a Benthos gravity corer (Benthos Inc., Falmouth, Mass.). Samples obtained in this manner exhibit little surface disturbance, although fine particles can be lost from the sediment surface during recovery of the Shipek bucket. The gear and shipboard procedures used were described by Gross et al. (1970).

Shipboard subsampling from the Shipek bucket is simple because the sediment is in a cylinder that can be easily removed from the sampler. For subsampling, an acetate tube 12 cm long and 8 cm in diameter is inserted into the sediment and withdrawn containing the subsample. Readings for acidity (pH),

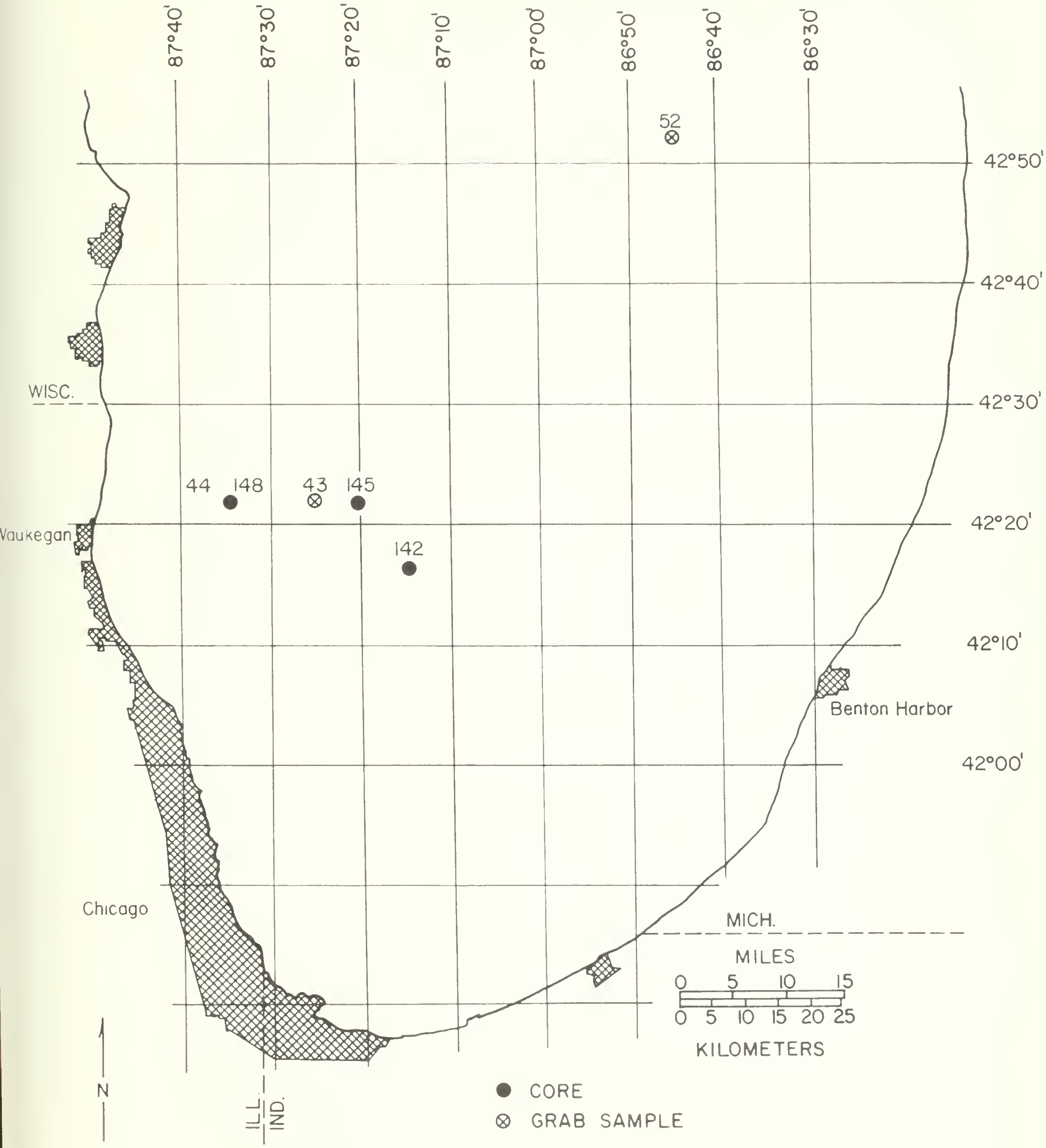

Fig. 1 - Location of Lake Michigan core and grab samples.

oxidation-reduction potential (E_h), and temperature are made at 0.2 cm, 1 cm, and 3 cm. The tube is then sectioned at appropriate intervals and the sections frozen for subsequent analysis.

Cores obtained from the Benthos sampler are frozen in a vertical position on board ship to prevent mixing of the upper few centimeters of sediment during transport. In the laboratory, frozen cores are freed from the plastic core liners, and the core is notched and cleaved with a plastic blade into the desired subsections. These sections are then rinsed with deionized water and thawed.

Samples for laboratory analysis are carefully drained of excess water after the fine material has settled and are immediately subsampled for particle-size and clay mineral determinations. Remaining portions of the samples are air-dried, ground to -100 mesh in high-alumina ceramic equipment, and used for the chemical analyses. Fifteen to 20 grams of moist sediment are needed for clay mineral analyses and a minimum of 20 g of air-dried sediment is required for chemical determinations. Trace elements are determined in the air-dried samples. Additional oven-drying at 110° C precedes determination of major and minor constituents.

Brief descriptions of the chemical, particle-size and mineralogic methods employed are given in the following paragraphs. The determinations were made in the laboratories of the Illinois State Geological Survey.

X-Ray Fluorescence

Aluminum, silicon, iron, calcium, magnesium, potassium, titanium, manganese, and phosphorus were determined by X-ray fluorescence following, in general, the method described by Rose, Adler, and Flanagan (1963). Samples and analyzed standards (0.125 g) were mixed with 0.125 g of lanthanum oxide and 1.000 g of lithium tetraborate and fused in graphite crucibles at 1000° C for 15 minutes. The glass fusion bead was crushed, ground to -325 mesh, and pressed into a pellet at 40,000 psi. The pellet, which also contained "Somar Mix" (Somar Laboratories, Inc., N. Y., N. Y.) as a binder, was used for determining all elements. Addition of the heavy-element absorber, lanthanum oxide, simplified calibration and increased accuracy by eliminating many of the enhancement and absorption effects common to X-ray emission methods.

A Norelco vacuum spectrometer equipped with a chromium X-ray tube was used for all determinations. Iron, titanium, and manganese were determined with a lithium fluoride crystal in an air path. An ethylenediamine ditartrate (EDDT) crystal in vacuum was used for determination of aluminum, silicon, potassium, calcium, and phosphorus. Corrections were made for second-order calcium interference in the phosphorus determination. Finally, magnesium was determined with an ammonium dihydrogen phosphate (ADP) crystal in vacuum. A background correction was made for each element, and all elements were calculated as their oxides. Relative precision values (coefficient of variation) for a single determination were as follows: ± 0.5 percent for SiO_2 and TiO_2; ± 1 percent for Al_2O_3, CaO, K_2O, Fe_2O_3; ± 2 percent for MgO; and ± 5 percent for P_2O_5 and MnO at the concentration levels encountered in this study.

Neutron Activation

Approximately 1 gram of air-dried sediment was accurately weighed into a 1.5 ml snap-cap "polyvial" and irradiated in the University of Illinois nuclear reactor for 1 hour at 5 by 10^{12} neutrons sec^{-1} cm^{-2} with appropriate synthetic standards. After an initial decay period of about one day, samples and standards were similarly counted at various positions above a 3-inch by 3-inch sodium iodide detector connected with a Nuclear-Chicago 400 channel analyzer. Aperiodically during a span of 3 or 4 weeks, gamma rays of the following isotopes were observed, decays were followed, and quantities present were estimated: 1.37 MeV (^{24}Na), 0.66 MeV (^{82}Br), 1.60 MeV (^{140}La), 0.89 MeV (^{46}Sc), and 2.50 MeV (^{60}Co). Relative precision (coefficient of variation) for a single determination was ± 10 percent to ± 15 percent.

Optical Emission

A large Bausch and Lomb Littrow spectrograph was used for the spectrographic analysis of sediments for beryllium, chromium, nickel, lead, and vanadium. Ground samples (15 mg) were mixed with 15 mg of graphite containing the internal standard, indium oxide (0.111%). Samples were packed into graphite electrodes and ignited in a 12 amp shorted D.C. arc. Spectra were recorded on S.A.-1 glass plates after attenuation through a seven-step (2 x steps) rotating sector placed at the 20μ primary slit.

Calibration was achieved by a series of synthetic standards excited and photographed in the same manner as the samples. Three series of silica-alumina base standards with ratios of 3:1, 4.25:1, and 8:1 were prepared, and the calibration most nearly matching the silica-to-alumina ratio of the unknown sample, as calculated from X-ray fluorescence data, was used for analysis. Matrix effects of the major elements were minimized by this procedure, whereas corrections for the effects of minor-element variations in samples were made by including indium as an internal standard. All intensities were corrected for background.

Analytical lines and precision values for these elements were:

Be	3130.4 A	± 15%	Pb	2833.1 A	± 15%
Cr	2677.2 A	± 10%	V	3183.98 A	± 15%
Ni	3414.8 A	± 10%	In	3256.1 A	

Atomic Absorption

A Beckman atomic absorption spectrophotometer with strip chart recorder was used for determination of cadmium, copper, and zinc. Sediment samples (0.5000 g) were digested in platinum crucibles with a mixture of 5 ml of concentrated hydrofluoric acid, 0.5 ml of perchloric acid, and 2 ml of nitric acid and evaporated to near dryness. Subsequently, they were dissolved in 5 ml of hydrochloric acid and deionized water was added to make a 50-ml volume. This solution was aspirated through a burner that had a slot aperture with high-solids capability, and air-acetylene was used as fuel. Scale expansion was used for cadmium and copper, and a background correction

was made for each element. Reagent blanks were carried throughout the procedure. For calibrations, high-purity salts of the metals dissolved in dilute acid solution were used. Analytical wave lengths, in millimicrons (mμ), used for analysis were 228.8 for cadmium, 324.7 for copper, and 213.9 for zinc. Precision for a single determination (coefficient of variation) was about ± 10 percent for the concentration levels encountered.

Boron

A colorimetric method similar to that described by Stanton and McDonald (1966) was used for determining boron. Ten ml of 2.5 N sulfuric acid and 4 ml of 5 percent hydrofluoric acid were added to 25 mg of the sample in a 4-ounce polyethylene plastic bottle. Deionized water was added to a predetermined 20-ml mark, the bottle tightly capped, and the contents allowed to stand overnight. Subsequently, deionized water was added to a predetermined 50-ml mark on the plastic bottle, and 10 ml of a 0.001 M solution of methylene blue and 25 ml of purified ethylene dichloride were then added. The bottle was shaken for a minimum of 1 minute, the layers allowed to separate, and 5 ml from the bottom layer was pipetted into a 25 ml volumetric flask. The solution was diluted to that volume with ethylene dichloride and the color intensity at 660μ was converted to boron concentration by comparison with a series of standards. A reagent blank was run with each series. Precision for a single determination was ± 5 percent.

Total Carbon

The determination of total carbon, including the carbon in carbonates, was made by burning a weighed sample (0.2 to 0.5 g) in a closed-system tube furnace at 1350° C. A stream of oxygen passing through the furnace assured complete conversion of all carbon to carbon dioxide and carried the combustion products from the furnace through a carbon dioxide absorption tube containing soda-asbestos. Prior to carbon dioxide absorption, sulfur dioxide and moisture were removed from the combustion products. After combustion was complete, the absorption bulb was removed, allowed to cool, and weighed to the nearest 0.1 mg. The increase in weight was due to absorbed carbon dioxide and is calculated to percent carbon for use in calculating organic carbon. This method is similar to that given in British Standard 1016 (1958), which is used for determining total carbon in coal and coke.

Inorganic Carbon and Organic Carbon

Inorganic carbon was determined by the common acid evolution-gravimetric method described by Maxwell (1968a). Inorganic carbon in 1.000 g of the sample was dissolved and carbon dioxide evolved by treatment with 1:1 hot hydrochloric acid in a flask fitted with a condenser. After purification, the carbon dioxide was absorbed in soda-asbestos and determined as the increase in weight of the absorption bulb. Inorganic carbon is reported as carbon dioxide.

Organic carbon was calculated by taking the difference between the percentage of total carbon and that of inorganic carbon.

TABLE 1 — CHEMICAL ANALYSES OF LAKE MICHIGAN GRAB AND CORE SAMPLES

	Constituents in Percent																	Trace Elements in Parts Per Million													
Depth (cm)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	CO_2	S	Ignition loss	Organic C	Total	<2μ Clay	B	Be	Br	Cd	Co	Cr	Cu	La	Ni	Pb	Sc	V	Zn	Depth (cm)
STATION 43, GRAB SAMPLE																															
0-2	72.6	0.30	6.27	2.51	0.07	2.74	4.54	0.84	1.96	0.02	1.71	5.51	—	8.56	1.34	99.50	—	—	ND	32	—	6	52	25	19	24	60	6	25	—	0-2
2-4	68.2	0.56	12.1	4.61	0.11	1.81	2.06	0.98	3.61	0.14	3.60	1.72	—	6.58	1.19	100.69	34	—	ND	≤49	—	8	55	42	38	40	30	14	42	—	2-4
4-6	62.1	0.58	12.2	4.70	0.11	2.98	2.59	0.93	3.67	0.11	3.93	4.22	—	9.4	1.25	98.33	48	—	6	≤44	—	—	—	—	44	—	—	15	—	—	4-6
6-8	58.6	0.61	12.3	4.93	0.10	3.55	3.68	0.85	4.51	0.09	4.90	3.81	—	10.04	1.33	98.31	49	—	ND	≤42	—	11	66	56	42	52	27	15	52	—	6-8
STATION 52, GRAB SAMPLE																															
0-2	72.1	0.28	6.57	2.87	0.06	2.79	3.04	0.55	2.01	0.04	2.37	3.92	—	7.92	1.36	97.62	—	—	—	50	—	5	47	30	18	32	58	6	29	—	0-2
2-4	78.7	0.37	8.17	3.02	0.10	1.52	1.33	0.74	2.62	0.01	2.46	1.25	—	4.74	1.03	100.48	24	—	—	≤28	—	7	44	29	25	36	22	8	37	—	2-4
4-6	72.5	0.40	10.5	3.70	0.11	1.31	1.61	0.73	3.07	0.04	3.27	1.34	—	5.66	1.05	99.63	36	—	—	≤34	—	10	58	34	30	44	24	10	44	—	4-6
6-8	69.5	0.49	10.1	3.77	0.11	2.06	2.18	0.70	3.13	0.05	3.34	2.45	—	7.16	1.37	98.44	44	—	—	≤41	—	8	58	37	31	44	28	11	49	—	6-8
STATION 145, 2-INCH CORE																															
0-8	58.7	0.58	12.8	6.28	0.13	4.09	2.28	0.74	3.86	0.37	5.10	2.49	0.02	9.57	1.96	99.49	54	80	2.2	66	10	18	64	51	45	38	26	12	70	106	0-8
23.7 31.6	43.5	0.43	11.0	3.94	0.06	5.04	13.5	0.57	3.11	0.21	4.10	12.78	0.19	18.61	1.54	100.23	64	62	1.8	29	14	18	57	41	38	35	20	10	52	97	23.7-31.6
67-73.8	44.4	0.40	10.2	3.63	0.08	5.36	14.0	0.59	2.90	0.20	2.98	14.83	0.02	18.73	0.90	100.61	56	60	2.0	≤19	9	17	54	37	32	33	18	9	64	92	67-73.9
138.3-152.3	54.9	0.56	17.8	7.30	0.11	4.91	2.55	1.55	3.85	0.17	4.74	0.36	0.01	6.02	0.91	99.81	87	63	1.8	<21	14	23	92	63	61	86	24	15	80	141	138.3-152.3
162.5-172.3	54.6	0.75	18.2	7.82	0.09	4.59	2.28	1.35	4.30	0.15	1.96	0.07	0.12	5.31	3.16	99.63	97	105	2.4	<19	13	35	76	61	67	66	25	16	74	138	162.5-172.3
229-257	54.9	0.67	17.7	6.16	0.09	5.32	2.53	1.20	4.51	0.13	4.11	2.11	Nil	6.34	0.12	99.55	92	121	2.4	<15	9	20	61	47	62	55	22	13	66	130	229-257
STATION 44, 3-INCH CORE																															
0-3	53.3	0.24	9.10	3.85	0.03	5.89	7.41	0.73	2.20	0.13	3.24	9.83	0.07	16.11	2.96	98.98	18	39	4	75	17	10	64	109	25	35	90	8	54	179	0-3
3-6	64.2	0.28	7.34	2.15	0.03	5.82	6.39	0.78	1.81	0.09	0.14	8.91	0.02	9.62	0.55	98.51	16	22	1.4	22	7	8	37	26	18	20	19	5	34	42	3-6
6-8	67.9	0.32	7.40	2.53	0.05	4.47	4.67	0.82	1.92	0.07	1.23	6.22	0.01	8.25	0.79	98.40	19	27	1.4	21	5	9	30	23	19	27	18	6	32	46	6-8
8-10.5	65.0	0.31	7.34	4.26	0.08	4.19	5.22	0.08	2.00	0.11	1.65	6.74	0.02	9.45	1.04	98.04	27	27	1.7	29	5	11	40	21	22	26	18	6	36	50	8-10.5
10.5-13.5	58.7	0.57	9.78	2.91	0.05	4.58	6.38	0.77	2.68	0.05	2.24	8.54	0.11	12.30	1.41	98.77	27	40	—	35	7	9	48	31	28	34	21	9	66	72	10.5-13.5
18.5-22	50.6	0.43	9.78	3.40	0.05	6.60	8.68	0.66	2.73	0.05	2.36	12.22	0.28	16.36	1.50	99.34	36	44	20	34	9	10	48	29	28	42	20	9	64	71	18.5-22
33-37	49.1	0.46	10.5	3.66	0.03	6.55	8.81	0.70	2.86	0.09	2.73	11.79	0.19	16.35	1.64	99.11	40	46	2.0	36	19	12	53	35	31	44	20	10	71	72	33-37
54-58.5	48.5	0.50	9.76	3.88	0.01	5.62	10.14	0.67	2.75	0.24	2.94	12.33	0.11	16.63	1.25	98.70	47	53	1.7	29	13	13	50	32	30	44	20	9	68	78	54-58.5
84-88	43.4	0.43	9.98	3.67	0.01	5.46	13.2	0.59	2.78	0.13	2.72	14.98	0.12	18.82	1.00	98.47	50	52	1.4	≤22	12	13	55	29	29	35	20	9	65	71	84-88
STATION 148, 2-INCH CORE																															
33.5-39	50.9	0.52	10.9	3.78	0.03	6.27	8.00	0.77	3.04	0.17	2.77	10.35	0.15	14.94	1.67	99.32	40	57	2.0	35	8	14	52	40	35	43	40	11	76	94	33.5-39
75.3-89.9	43.0	0.47	9.81	3.55	0.04	6.88	14.0	0.65	2.85	0.19	1.93	15.23	0.13	18.30	1.01	99.74	50	70	1.5	22	14	13	55	35	32	31	22	9	57	88	75.3-89.9
96.8-120.7	43.1	0.45	10.1	3.30	Nil	6.07	13.0	0.65	2.65	0.14	3.41	15.83	0.12	20.29	0.93	99.75	48	58	1.7	21	9	15	50	25	33	34	20	9	54	100	96.8-120.7
193.3-205.5	43.2	0.47	9.26	2.88	Nil	8.28	13.1	0.75	2.44	0.11	1.91	16.90	0.02	19.48	0.65	99.97	34	44	1.4	≤10	13	13	44	28	32	36	16	8	56	63	193.3-205.5
317.7-325.8	46.7	0.33	7.65	2.32	Nil	7.41	13.2	0.80	2.32	0.12	1.22	17.53	0.05	19.11	0.31	99.96	35	35	1.0	< 7	10	10	34	26	24	29	16	6	48	50	317.7-325.8
STATION 142, 3-INCH CORE																															
0-4	60.8	0.39	8.98	3.11	0.04	4.61	4.88	0.74	2.48	0.24	3.60	7.20	0.03	12.39	1.56	98.66	44	43	3.2	42	16	13	56	38	27	41	44	8	58	93	0-4
4-7	44.0	0.40	10.7	3.53	0.04	5.44	12.9	0.63	2.92	0.09	3.54	13.56	0.03	18.16	1.03	98.81	71	62	1.8	26	16	18	50	40	32	40	21	10	66	70	4-7
7-10	44.3	0.43	11.2	3.50	0.06	4.73	13.1	0.59	2.85	0.11	3.89	13.54	0.02	18.12	0.67	98.99	69	63	2.4	26	15	17	53	38	33	46	20	10	68	68	7-10
10-13	45.0	0.44	10.2	3.49	0.09	4.28	13.7	0.62	2.91	0.13	3.90	13.43	0.02	18.03	0.68	98.89	65	66	1.7	24	11	18	50	38	32	47	19	9	78	65	10-13
19-23	53.1	0.42	9.07	3.04	0.03	4.48	9.87	0.74	2.45	0.19	3.16	11.63	0.01	15.14	0.34	98.53	41	51	1.7	14	9	13	41	39	29	38	18	8	69	54	19-23
51-55	52.9	0.62	14.5	4.88	0.09	4.31	4.35	0.98	3.83	0.23	5.79	6.41	0.02	12.51	0.29	99.20	84	43	2.0	≤13	10	20	51	49	48	60	20	12	72	52	51-55

Dash = not determined
ND = not detected

Analyses were made in the laboratories of the Illinois State Geological Survey by J. K. Kuhn and L. R. Henderson (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MnO, MgO, CaO, K_2O, and P_2O_5), R. R. Ruch (Br, Co, La, Sc, and Na_2O), J. A. Schleicher (Be, Cr, Ni, Pb, and V), D. B. Heck (B, Cd, Cu, and Zn), L. R. Camp (CO_2, S, and ignition loss), and C. W. Beeler (total carbon).

TABLE 2—MINERALOGY OF THE CLAY-SIZE FRACTION OF LAKE MICHIGAN CORE 145 REVEALED BY X-RAY DIFFRACTION

(diffraction effects in parts in 10)

	Nonclay minerals*						Clay minerals*				Expandable clay minerals*			Calcite-dolomite ratio
Depth (cm)	A	KF	PF	D	Ca	Qtz	I	C	K	MX	V	M	Other	
0-8		P	P			P	3-4	3-4		3	2		8	
23.7-31.6					P	P	3-4	3		3	3		7	
67-73.8				P	P	P	2	1-2		6	2-3		7-8	2½-1
138.3-152.3		P	P			P	4	4		2-3	5		5	
162.5-172.3	P	P	P			P	3	3	1	3	1		9	
229-257	P	P	P	P		P	3-4	3-4	2	2-3	2		8	

TABLE 3—MINERALOGY OF THE CLAY-SIZE FRACTION OF LAKE MICHIGAN CORES 44 AND 148 REVEALED BY X-RAY DIFFRACTION

(diffraction effects in parts in 10)

	Nonclay minerals*						Clay minerals*				Expandable clay minerals*			Calcite-dolomite ratio
Depth (cm)	A	KF	PF	D	Ca	Qtz	I	C	K	MX	V	M	Other	
0-3		?	?	P		P	2-3	2-3		5	1		9	
3-6				P		P	3	2		4	1		9	
6-8				P		P	3-4	2		4				
8-10.5				P		P	2-3	1-2		6	1		9	
10.5-13.5						P	2-3	2		4-5	1-2		8-9	
18.5-22				P		P	3	2		4-5	1-2		8-9	
33-37				P		P	3	3		4-5	1-2		8-9	
54-58.5				P		P	4	2-3		3	2		8	
75.3-89.9‡		?	?	P	P	P	3-4	1-2		5	1		9	3-2
84-88				P	P	P	4	2		4	4		6	1-1
96.8-120.7‡		?	?	P	P	P	2-3	1-2		6	1		9	1-1
193.3-205.5‡	P	P	P	P	P	P	2-3	2	1	4	1-2		8-9	1-3
317.7-325.8‡	P	P	P	P	P	P	4	2-3	1	3	2		8	1-2

*A = Amphibole
KF = Potash feldspar
PF = Plagioclase feldspar
D = Dolomite
Qtz = Quartz

Ca = Calcite
I = Illite
C = Chlorite
K = Kaolinite

MX = Expandable clay minerals
V = Vermiculite
M = Montmorillonite
P = Present
‡ = Samples from core 148

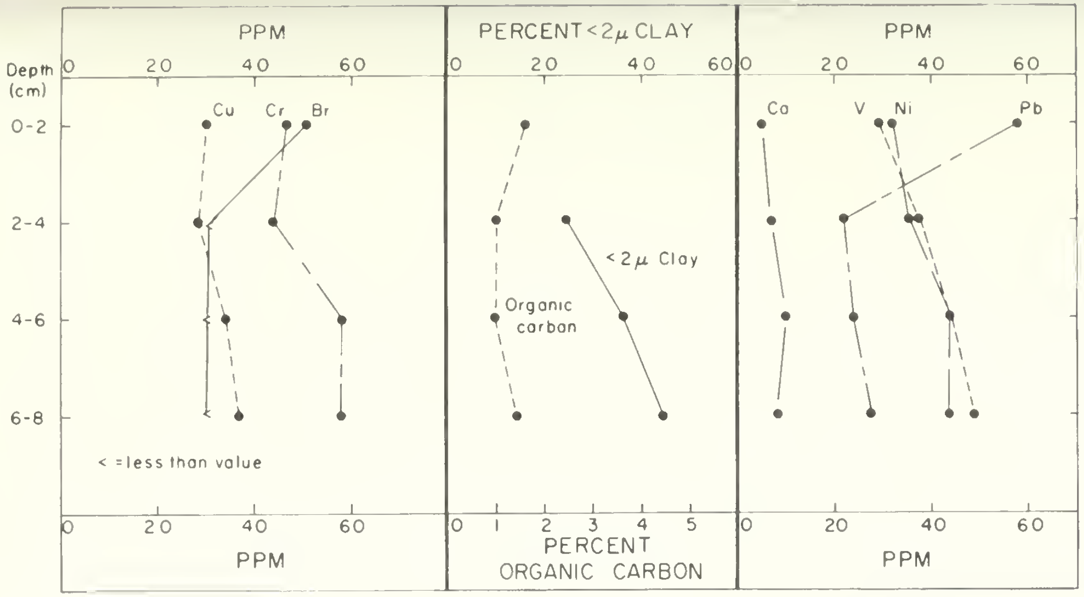

Fig. 2 - Distribution of trace elements, organic carbon, and <2μ clay in Lake Michigan grab sample No. 52.

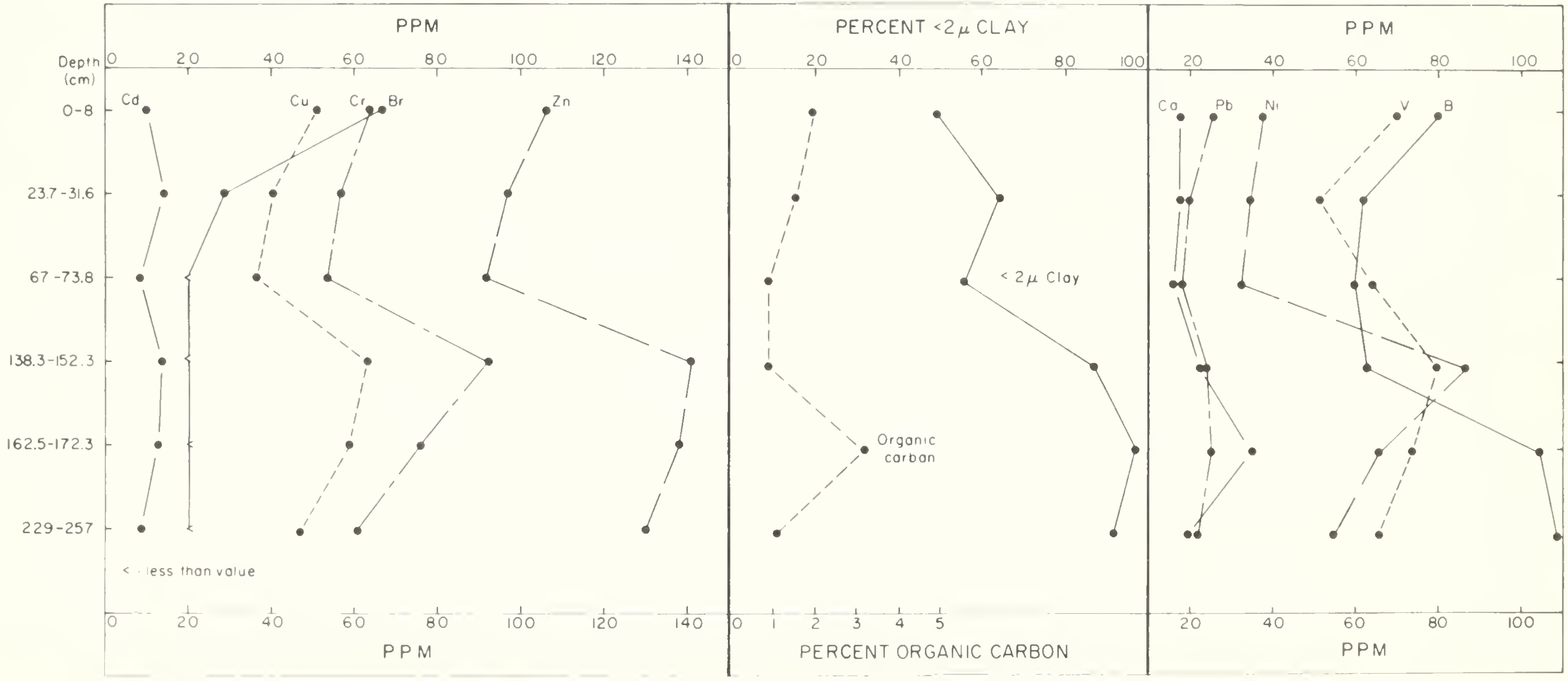

Fig. 3 - Distribution of trace elements, organic carbon, and <2μ clay in Lake Michigan core No. 145.

Total Sulfur

Sulfide sulfur was determined by digesting 3.000 g of the sample in 15 ml of a 1:4 mixture of saturated bromine water and carbon tetrachloride for 30 minutes. Concentrated nitric acid (15 ml) was added and the flask slowly heated to dryness. Dissolved silica from the sample was then dehydrated with 20 ml of concentrated hydrochloric acid. After evaporation to dryness, 50 ml of 10 percent hydrochloric acid was added to the residue and this solution allowed to stand 2 hours. Aluminum dust was added to the solution to reduce the iron and, after an additional 2 hours, the solution was brought to a boil and cooled. No more than 20 minutes later, the solution was filtered and the filtrate diluted to 350 ml with deionized water. Subsequently, the solution was reheated and the barium sulfate precipitated with 10 ml of 10 percent barium chloride in 5 percent hydrochloric acid. The solution was boiled for 1 hour, allowed to stand overnight, and filtered. The barium sulfate precipitate was ignited at 1000° C, weighed, and the amount of sulfur in the precipitate was reported as percentage of sulfur in the sediment. A similar procedure for determining sulfide sulfur has been described by Maxwell (1968).

Moisture

Moisture for these sediments was calculated by taking the difference between the ignition loss and carbon dioxide plus sulfur plus organic carbon.

Clay-Size Fraction

The less than 2-micron clay fraction was determined by conventional pipette analysis. Deionized water was added to an amount of the moist sediment equivalent to 10 g of oven-dried (100° C) material and agitated in an Osterizer. A deflocculating solution was added and the suspension was allowed to stand overnight in a bath with a constant temperature of 30° C. A 10 ml aliquot was then taken at the depth and time indicated for removal of the less than 2-micron clay fraction. This aliquot was evaporated to dryness, weighed, and the percentage of clay calculated to the oven-dry weight basis.

X-Ray Diffraction of Minerals

X-ray diffraction methods were used for determining the mineralogic composition of the less than 2-micron clay fraction of the Lake Michigan sediments. Clay samples were prepared for analysis by dispersing and deflocculating 1 gram of material in 50 ml of distilled water. Suspensions were allowed to stand for 28 minutes, after which aliquots were removed from the upper 5 mm, placed on glass slides, and dried.

Slides were X-rayed at 2° two-theta per minute and then placed in ethylene glycol for at least 5 days. They were subsequently X-rayed in the same manner as the untreated slides. Following the glycol treatment, slides were heated at 343° C for an hour and again X-rayed.

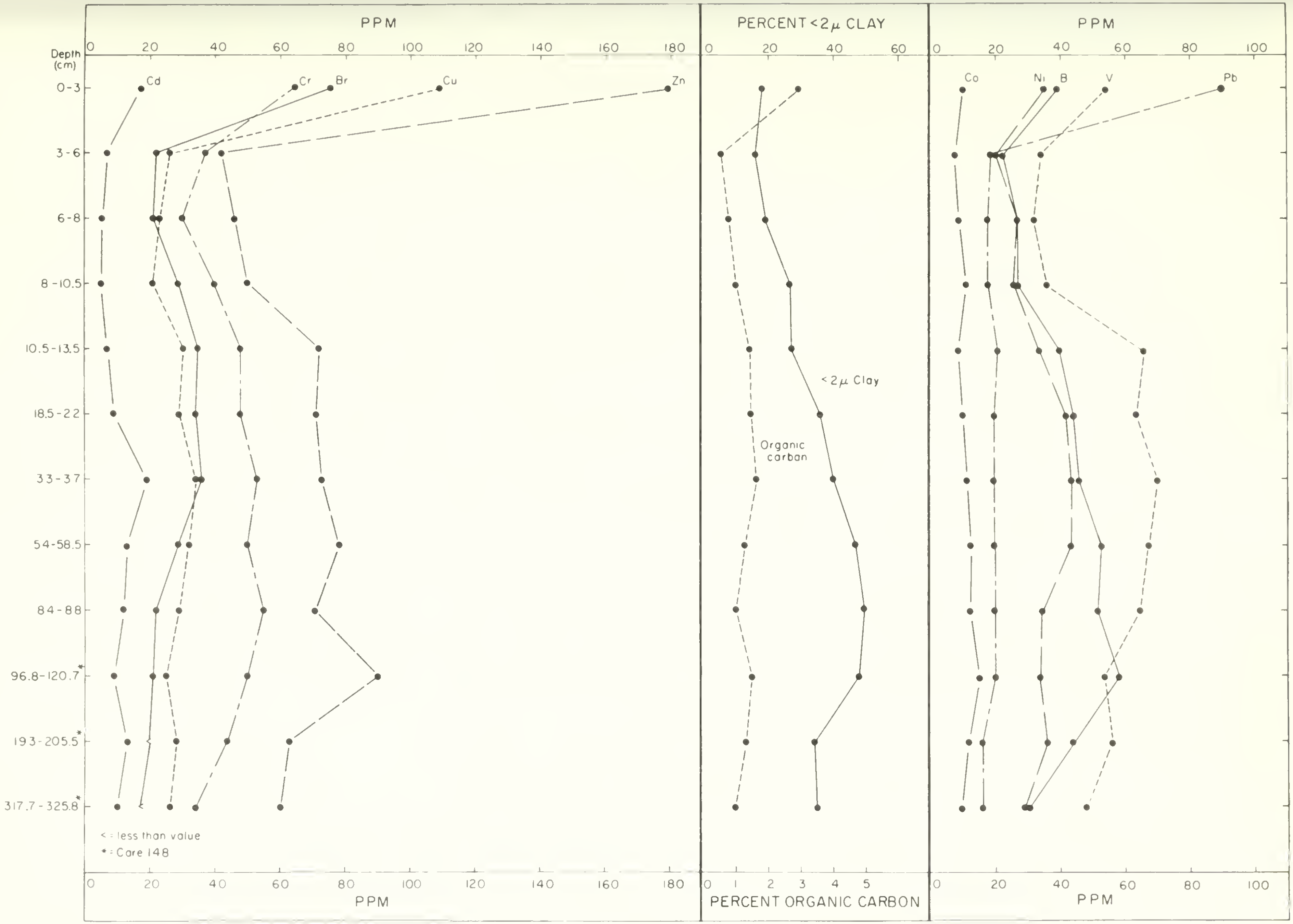

Fig. 4 - Distribution of trace elements, organic carbon, and < 2μ clay in Lake Michigan cores No. 44 and 148.

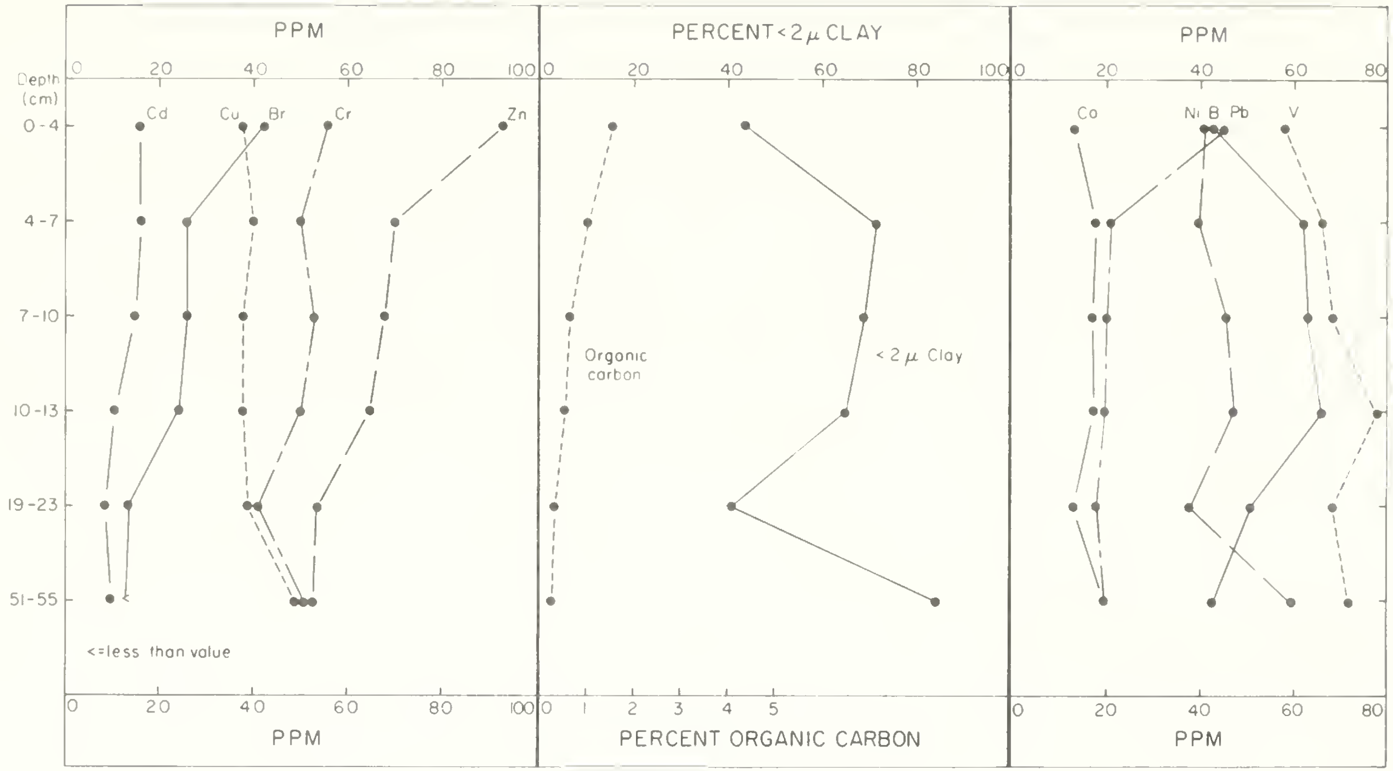

Fig. 5 - Distribution of trace elements, organic carbon, and <2 μ clay in Lake Michigan core No. 142.

Illite was used as the reference clay mineral. The area under the 8.8° two-theta illite peak of the diffractogram for the glycolated slide was used for calculating the ratios of the other clay minerals, which were determined from the glycolated slide after it was heated. Ratios of expandable clay minerals and illite were determined by the difference in areas of the 8.8° two-theta peaks on diffractograms of the glycolated and heated slides. The ratio of illite to chlorite was calculated from areas of the 17.9° two-theta peak on diffractograms obtained from the glycolated slide and the area of the 18.7° two-theta peak after the slide was heated. Kaolinite-to-chlorite ratios were determined by X-raying slides (that had been heated) from 24.5° to 25.5° two-theta at one-fourth or one-half degrees per minute. The fourth order diffraction effects of chlorite near 25° two-theta were multiplied by two to obtain the ratio of chlorite to kaolinite. This ratio was then multiplied by the ratio of the third-order chlorite (18.7° two-theta) and the second-order illite peaks (17.9° two-theta) to obtain ratios between kaolinite, illite, chlorite, and expandable clay minerals.

Expandable clay minerals were separated where possible and recorded as ratios of the different expandable clay minerals. Vermiculite was calculated from the difference between the 12.5° two-theta peak heights of the glycolated and heated samples. Montmorillonite was determined on the glycolated slide from the area of the 5° two-theta peak of this diffractogram divided by four. The intensity of this peak was four times that of the 9° two-theta peak obtained after the slide is heated and after collapse of the montmorillonite lattice. All of the clay-mineral data are ratios of diffraction effects and are not considered as percentages.

RESULTS AND DISCUSSION

Locations for the five stations sampled in southern Lake Michigan are shown in figure 1. Descriptions of the samples analyzed at various depths are given in the appendix; complete stratigraphic descriptions of cores for stations 145, 44, and 148 are given by Gross et al. (1970). Station 44 is equivalent to station 148, the sample from 148 having been taken to permit deeper penetration of the sediment than is possible with the Benthos corer used for station 44.

Results of chemical determinations for major, minor, and trace constitutents at various depth intervals in the sediments are presented in table 1. Mineralogic data at the same depth intervals of cores 145, 44, and 148 are given in tables 2 and 3.

The concentration of each trace element (except beryllium, lanthanum, and scandium) is plotted against depth in figures 2, 3, 4, and 5. For comparative purposes, the percentages of the less than 2-micron clay fraction and the organic carbon are also graphically displayed. The trace elements have been separated into two groups for clarity of presentation.

Data for the grab sample obtained at station 52 are incomplete (table 1; fig. 2) because the sample was too small for the determination of

some of the trace elements and the less than 2-micron clay in the 0-2 cm interval. Grab sample 43 also was too small for complete analysis, and trace element data from it are not plotted. In figure 2 the distribution of trace elements shows an accumulation of lead and bromine (probably bromide in the sediments) in the upper 2 cm. These data were the first indication that the trace element content of the sediments varies within the upper few centimeters. Analyses for the major elements in grab samples 43 and 52 support this observation (see data for Al_2O_3 and Fe_2O_3, table 1) despite the fact that some fine-textured surface material may have been lost during recovery of the Shipek grab samples.

Because the intervals between samples taken from core 145 were so large, interpretation of the trace element distribution patterns (fig. 3) is difficult. In the first 75 cm of the core, the patterns for trace elements zinc, boron, vanadium, chromium, bromine, and copper are similar to the distribution of organic carbon. At the 138.5-to 152.3-cm interval, however, trace elements zinc, nickel, chromium, vanadium, and copper increase sharply, and the increase corresponds to the large increase in clay content at that interval.

The distribution of trace elements in cores 44 and 148 are shown in figure 4. These two cores taken from the same station constitute the longest section of core analyzed to date. This station is closer to shore (12 miles off Waukegan, Illinois) than the others, and the upper 3 cm of core 44 contains less clay but more organic matter than the same interval does in the other cores. Accumulation of trace elements zinc, copper, lead, bromine, and chromium is pronounced in the first 3 cm of this core, which may be due to a higher organic content and/or a greater incidence of pollution in the near-shore environment. If a relation does, in fact, exist between the amount of organic carbon and concentrations of certain trace elements, then variations in organic matter content would have a major influence upon the distribution of trace elements in the sediments. Most trace elements in deeper portions of cores 44 and 148 are apparently related to the amount of clay present.

Core 142 (fig. 5) also shows an accumulation of zinc, lead, bromine, and possibly chromium in the upper 4 cm, despite the fact that clay content is much lower near the surface of this core than at deeper levels. The close relation between boron and clay content is pronounced in core 142, as it is to a somewhat lesser degree in cores 44 and 148 (fig. 4).

Additional chemical data from other locations will be published in subsequent numbers of the Illinois State Geological Survey's Environmental Geology Notes series. In addition, multifactorial analyses will be made for possible correlations of the abundance of trace elements with such variables as organic carbon, amount of clay, depth, and geographic location.

SUMMARY

The data derived from our analyses are the initial step for establishing what concentrations of trace elements in Lake Michigan sediments can be considered as natural concentrations, the standard against which present

pollution can be measured. As analyses of additional samples are completed, any unusual concentrations of trace elements in the sediments may thus be identified.

As our data represent only a small portion of the lake bottom, they should not be used to form general, and perhaps unwarranted, conclusions regarding the occurrence of trace elements in Lake Michigan sediments. However, certain trends are evident regarding the distribution of the trace elements in these particular sediments analyzed.

Variations in concentrations of both major and trace constituents occur within the first few centimeters of sediment below the sediment-water interface. These variations are relatively large, and our findings show they cannot be seen in sufficient detail unless the upper 10 centimeters of sediment are subsampled into units no more than 2 or 3 centimeters thick.

The trace elements lead, bromine, zinc, nickel, and chromium accumulate in the top few centimeters of the sediments. Concentrations tend to vary with the amount of organic carbon present in the sediments in that interval.

In contrast, in the deeper sediments many of the trace element concentrations vary with the amount of less than 2-micron clay present.

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APPENDIX

DESCRIPTIONS OF LAKE MICHIGAN SAMPLES

Descriptions by J. A. Lineback, D. L. Gross, and N. J. Ayer. Compiled by J. A. Lineback. For more complete descriptions see Gross et al., 1970.

STATION 43, GRAB SAMPLE

42° 21.8' N, 87° 25.2' W; 20 miles east of Waukegan, Illinois, 305 feet of water; pH 7.1; E_h 0.5 to 0.8.

	Thickness (cm)
Organic layer	0-2
Mud, clayey, organic-rich	2-4
Mud, clayey, organic-rich	4-6
Mud, clayey, organic-rich	6-8

STATION 52, GRAB SAMPLE

42° 52.7' N, 86° 42.5' W; approximately 65 miles northeast of Waukegan, 290 feet of water; pH 7.2; E_h 2.0 to 2.5.

	Thickness (cm)
Silt, organic-rich	0-2
Clay, sandy, yellowish dark gray	2-4
Clay, sandy, yellowish dark gray	4-6
Clay, sandy, yellowish dark gray	6-8

STATION 145, 2-INCH CORE

42° 21.8' N, 87° 20.3' W; 24 miles east of Waukegan, Illinois 346 feet of water; pH 7; E_h 1.9.

	Thickness (cm)
Clay, sandy, silty, brownish gray, soft; contains a few compact layers 1 mm thick	0-8

STATION 145, 2-INCH CORE (Continued)

	Thickness (cm)
Clay, silty, gray with black mottling and layers of black sediment	23.7-31.6
Clay, silty, brownish gray	67-73.8
Clay, dark gray mottled with indistinct bands of black clay	138.3-152.3
Clay, reddish brown	162.5-172.3
Clay, reddish gray	229-257

STATION 44, 3-INCH CORE

42° 21.8' N, 87° 34.5' W; 12 miles east of Waukegan, Illinois; 238 feet of water; pH 7.1; E_h 0.5 to 0.8. Frozen core with stratigraphic units somewhat disturbed.

	Thickness (cm)
Silt, sandy, dark brownish gray	0-3
Silt, sandy, dark brownish gray	3-6
Silt, sandy, brownish gray	6-8
Silt, sandy, clayey, yellow-brown	8-10.5
Silt, sandy, clayey, brownish gray	10.5-13.5
Silt, clayey, brownish gray	18.5-22
Silt, clayey, brownish gray	33-37
Clay, silty, brownish gray	54-58.5
Clay, silty, brownish gray	84-88

STATION 148, 2-INCH CORE

42° 21.8' N, 87° 34.5' W; 12 miles east of Waukegan· 240 feet of water; no pH or E_h taken at this site.

	Thickness (cm)
Silt, clayey, dark gray with darker gray mottling	33.5-39.0

STATION 148, 2-INCH CORE (Continued)

	Thickness (cm)
Clay, silty, dark brownish gray with a few very dark gray mottlings and indistinct layers ..	75.3-89.9
Clay, silty, light brownish gray fossils and a few black mottlings	96.8-120.7
Silt, clayey, brownish gray to brown, faintly laminated	193-205.5
Till, sandy, clayey, silty, brownish gray, clay pebbles and angular rock fragments	317.7-325.8

STATION 142, 2-INCH CORE

42° 16.2' N, 87° 14.8' W; 31 miles east-southeast of Waukegan, 300 feet of water; pH 7.0; E_h 1.5 to 2.0. Five centimeters of black silt over brown clay. This core was frozen and the stratigraphic units disturbed. It appears to have consisted mainly of sandy, silty clay.

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